

# Transient episodes of mild environmental oxygenation and oxidative continental weathering during the late Archean

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It is not known whether environmental O<sub>2</sub> levels increased in a linear fashion or fluctuated dynamically between the evolution of oxygenic photosynthesis and the later Great Oxidation Event. New rhenium-osmium isotope data from the late Archean Mount McRae Shale, Western Australia, reveal a transient episode of oxidative continental weathering more than 50 million years before the onset of the Great Oxidation Event. A depositional age of  $2495 \pm 14$  million years and an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.34 \pm 0.19$  were obtained for rhenium- and molybdenum-rich black shales. The initial  $^{187}\text{Os}/^{188}\text{Os}$  is higher than the mantle/extraterrestrial value of 0.11, pointing to mild environmental oxygenation and oxidative mobilization of rhenium, molybdenum, and radiogenic osmium from the upper continental crust and to contemporaneous transport of these metals to seawater. By contrast, stratigraphically overlying black shales are rhenium- and molybdenum-poor and have a mantle-like initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.06 \pm 0.09$ , indicating a reduced continental flux of rhenium, molybdenum, and osmium to seawater because of a drop in environmental O<sub>2</sub> levels. Transient oxygenation events, like the one captured by the Mount McRae Shale, probably separated intervals of less oxygenated conditions during the late Archean.

## INTRODUCTION

Multiple lines of geochemical evidence from sedimentary rocks point to the production and accumulation of photosynthetic O<sub>2</sub> in surface environments since at least 3 billion years ago (Ga) (1–7). In contrast, sulfur mass-independent fractionation (S-MIF) indicates that Archean atmospheric O<sub>2</sub> levels were predominantly below 0.001% of present atmospheric levels (PALs) (8, 9). However, transiently higher O<sub>2</sub> levels are possible if crustal recycling of S-MIF signatures is taken into account (10). Therefore, evidence for O<sub>2</sub> production during Archean time may represent one of several scenarios. One possibility is that small linear stepwise increases in atmospheric O<sub>2</sub> allowed mild oxygenation and oxidative continental weathering to occur continuously and with increasing intensity in the several hundred million years before the first major accumulation of O<sub>2</sub> in the atmosphere [the ca. 2.4- to 2.1-Ga Great Oxidation Event (GOE)]. Alternatively, the GOE was preceded by a nonlinear pattern of initial oxygenation characterized by multiple transient oxygenation and oxidative weathering events (“whiffs” of O<sub>2</sub>) (1, 7). Nonlinear fluctuations in Earth surface redox conditions may have also been driven by variations in the relative fluxes of reducing gases, such as biogenic methane (11–14). Distinguishing between these hypotheses is critical for understanding the dynamics of planetary oxygenation on Earth and ultimately the evolution of complex life (7).

The 2.5-Ga Mount McRae Shale (Hamersley Basin, Western Australia) highlights the difficulties inherent in identifying changes in ancient environmental O<sub>2</sub> levels. Black shales from the upper Mount McRae Shale record an episode of high Mo and Re concentrations (Fig. 1) that

suggest oxidative mobilization of these metals from the upper continental crust, followed by their transport as oxyanions to seawater (1). Increased Mo and Re concentrations may capture a transient increase in oxidative continental weathering, possibly associated with a rise in atmospheric O<sub>2</sub> levels, and the subsequent decrease in Mo and Re concentrations may reflect a return to a lower redox state (1). However, sedimentary Fe speciation shows that the Mo and Re concentrations rise in phase with a shift in local bottom water redox conditions from anoxic and Fe<sup>2+</sup>-rich (ferruginous) to anoxic and H<sub>2</sub>S-rich (euxinic) (15). Because the magnitude of Mo and Re enrichment in marine sediments is influenced by local bottom water redox conditions, organic carbon export fluxes, and sedimentation rates (16, 17), the elevated Mo and Re concentrations may reflect changes in local depositional conditions against a backdrop of mild environmental O<sub>2</sub> levels (1). Both scenarios are consistent with stratigraphic trends in S, N, Mo, U, and Se isotope data in the Mount McRae Shale (1, 2, 15, 18–21). Distinguishing between these two possibilities is critical in understanding the controls on possible O<sub>2</sub> production and accumulation before the GOE.

To determine whether the chemostratigraphic trends in the Mount McRae Shale capture continuous or transient oxidative continental weathering, and to directly test recent challenges to the geochemical evidence for pre-GOE oxygenation (22), we turned to the Re-Os isotope system. An isochron regression of Re-Os data from temporally related black shales yields a depositional age, and the initial  $^{187}\text{Os}/^{188}\text{Os}$  records the local seawater  $^{187}\text{Os}/^{188}\text{Os}$  ratio at the time of deposition (23, 24). Seawater  $^{187}\text{Os}/^{188}\text{Os}$ , in turn, reflects a time-varying balance between radiogenic and unradiogenic Os fluxes to the ocean. Modern seawater has a highly radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  of ca. 1.06 (25, 26) due to riverine runoff of radiogenic Os derived from oxidative continental weathering (~1.5) (27). A subordinate flux of unradiogenic Os originates from dissolution of cosmic dust and hydrothermal alteration of ultramafic oceanic rocks (~0.13) (28–30). On continental margins, organic-rich sediments are an Os sink and directly record local seawater  $^{187}\text{Os}/^{188}\text{Os}$  (31). Hence, the initial  $^{187}\text{Os}/^{188}\text{Os}$  from ancient black

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shales can be used to infer temporal changes in the Os fluxes to seawater from mantle/extraterrestrial sources versus those tied to oxidative continental weathering.

## RESULTS

We measured Re and Os isotope data (table S1) for eight Re- and Mo-rich black shale samples of the Mount McRae Shale from 148.09- to 148.15-m depth in the ABDP-9 core (Archean Biosphere Drilling Project core #9), which previously yielded geochemical evidence for oxidative continental weathering and possible surface ocean oxygenation (1, 2, 15, 18–21). The analytical methods are described in Materials and Methods. Regression of the eight analyses (plus four replicate analyses) together with four previous Re-Os analyses from 145.22, 146.08, 147.10, and 148.32 m in ABDP-9 (1) yields a 16-point Re-Os age of  $2495 \pm 14$  million years ago (Ma) (the  $2\sigma$  age uncertainty includes a 0.31% uncertainty on the  $^{187}\text{Re}$  decay constant) and an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.34 \pm 0.19$  (Fig. 2).

## DISCUSSION

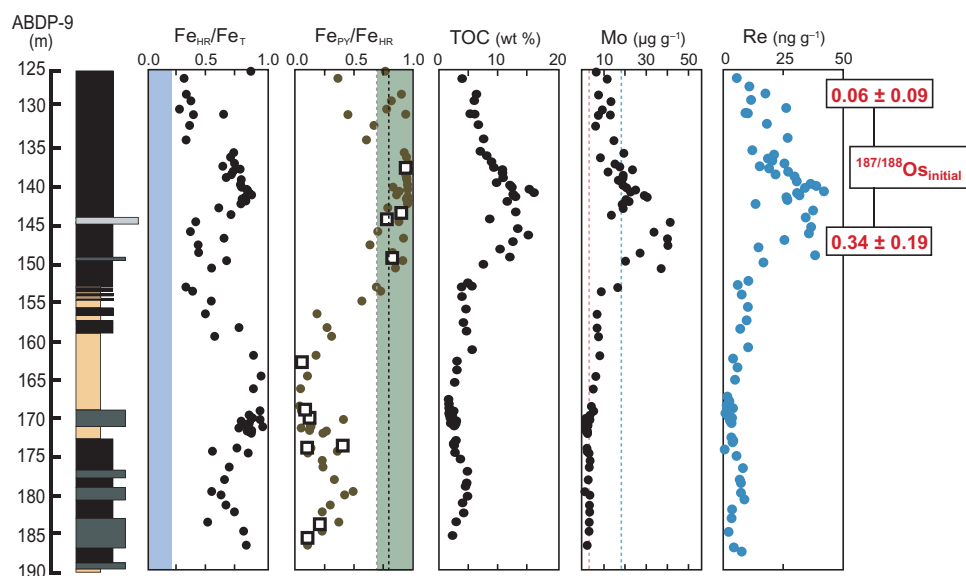
### Osmium isotope evidence for oxidative continental weathering at 2.5 Ga

Recently, a sophisticated set of petrographic analyses was used to suggest that the purported geochemical evidence for oxidative continental weathering recorded by the Mount McRae Shale is instead entirely a product of metasomatic overprints (22). However, the new Re-Os black shale age of  $2495 \pm 14$  Ma for 145.22 to 148.32 m is statistically identical to a Re-Os black shale age of  $2495 \pm 20$  Ma from 128.71 to 129.85 m in the ABDP-9 core (1) and to an U-Pb zircon age of  $2504 \pm 5$  Ma from a tuffaceous bed within the Mount McRae Shale (32). The agreement be-

tween the Re-Os and U-Pb ages is an important observation, given the possibility that sedimentary strata of the Pilbara Craton have been chemically altered by postdepositional hydrothermal fluid flow (33). Our new data confirm that metasomatic processes have not noticeably perturbed the Re-Os system in the Mount McRae Shale subsequent to deposition at  $\sim 2.5$  Ga.

Given that Mo is a redox-sensitive, siderophilic, and chalcophilic trace metal that should be characterized by postdepositional chemical mobility and overprints similar to those of Re and Os, it is likely that Mo has also escaped significant metasomatic alteration. In any case, Re enrichment alone provides strong evidence for oxidative continental weathering, and the likely preservation of its primary (depositional) signal is directly linked to the demonstrably unperturbed Re-Os system. A primary depositional signal is also supported by strong correlations between total organic carbon and both Mo and Re concentrations, an expected signature of oxidative mobilization and transport of soluble  $\text{MoO}_4^{2-}$  and  $\text{ReO}_4^-$ , and subsequent removal of these metals to anoxic sediments (1).

Most significantly, the initial  $^{187}\text{Os}/^{188}\text{Os}$  value of the Re-Os regression is statistically higher than the mantle/extraterrestrial value of 0.11 at 2.5 Ga (the modern value of 0.13 is higher because of  $^{187}\text{Re}$  decay to  $^{187}\text{Os}$  since 2.5 Ga). This observation indicates that local paleo-seawater  $^{187}\text{Os}/^{188}\text{Os}$  was higher than the mantle value and hence that oxidative continental weathering supplied radiogenic Os from the upper crust to Hamersley Basin seawater. Previously, the oldest known example of radiogenic Os delivery to seawater was captured by sedimentary rocks of the Huronian Supergroup, deposited in the aftermath of a widespread Paleoproterozoic glaciation at ca. 2.3 Ga (34). All other black shales between 2.7 and 2.0 Ga ( $n = 5$ ) yield initial  $^{187}\text{Os}/^{188}\text{Os}$  values from Re-Os isochron regressions that are indistinguishable from the mantle/extraterrestrial value (1, 35–38). The Mount McRae Shale thus captures the oldest known example to date of a radiogenic continental Os contribution



**Fig. 1. Stratigraphic and chemostratigraphic trends in the Mount McRae Shale.** Ratios of highly reactive iron ( $\text{Fe}_{\text{HR}}$ ) to total iron ( $\text{Fe}_{\text{T}}$ ) greater than 0.22 (blue bar) point to anoxic bottom waters, whereas the ratio of pyrite iron ( $\text{Fe}_{\text{PV}}$ ) to  $\text{Fe}_{\text{HR}}$  distinguishes between ferruginous (<0.7 to 0.8) and euxinic (>0.7 to 0.8; green bar) conditions (59). Filled circles show data from Reinhard *et al.* (15), recalculated according to Raiswell *et al.* (60), whereas open squares show results from quantitative x-ray diffraction analysis (60). Black shales dated using Re-Os geochronology were deposited from anoxic and euxinic bottom waters. Red and blue dashed lines indicate average Mo concentration in Archean and Proterozoic euxinic black shales, respectively (1). TOC, total organic carbon.

to seawater and represents the most direct evidence for chemical interaction between photosynthetic O<sub>2</sub> and crustal rocks at Earth's surface.

Continental sulfide minerals probably supplied radiogenic Os to Hamersley Basin seawater. The similar ionic size and charge of Re<sup>4+</sup> and Mo<sup>4+</sup> enable significant uptake of Re into molybdenites during crystallization. The average Re concentration of 71 ppm in Archean molybdenite is four orders of magnitude higher than in bulk silicate crust (39). Hence, molybdenites contain high <sup>187</sup>Os concentrations generated by in situ radioactive decay of <sup>187</sup>Re. Iron-bearing sulfide minerals (for example, pyrite, arsenopyrite, and pyrrhotite) have Re concentrations (parts-per-billion levels) that are orders of magnitude lower than those of molybdenite but are relatively more abundant in the continental crust (24, 35, 40, 41). Relationships between dissolved SO<sub>4</sub><sup>2-</sup>, Re, and Mo concentrations in modern rivers suggest that oxidative continental weathering of iron-bearing sulfide minerals is an important source of Re and Mo to modern seawater (42). The oxidative weathering of black shales (which hosts Re and Os in organic matter

and pyrite) may be a major supplier of Re but is a relatively minor source of Os and Mo to modern seawater (42, 43).

Other continental minerals (for example, silicates) were not likely to be major sources of Re, Mo, and Os to late Archean seawater. Uranium concentrations in the Mount McRae Shale are consistently low (indicating limited oxidation of U<sup>4+</sup> to U<sup>6+</sup> and thus low seawater U concentrations), and U is primarily held in nonsulfide minerals (for example, silicates, phosphates, zircon, and uraninite) that oxidize more slowly relative to sulfides (1, 44, 45). Hence, oxidative mobilization of Re, Mo, and radiogenic Os from continental sulfide minerals followed by their transport to seawater together as metal oxyanions provides a coherent and compelling explanation for the high Re and Mo enrichments and elevated seawater <sup>187</sup>Os/<sup>188</sup>Os captured by the black shales at 145.22 to 148.32 m in the ABDP-9 drill core (Fig. 1).

### Atmospheric O<sub>2</sub> concentrations at 2.5 Ga

Mass-balance modeling places constraints on the relative importance of the continental Os flux during deposition of the Mo- and Re-rich shales at 145.22 to 148.32 m. Compared with today, the Archean continental crust was smaller in volume (46) and had lower <sup>187</sup>Os/<sup>188</sup>Os because less radiogenic <sup>187</sup>Os had accumulated from <sup>187</sup>Re decay. Early Paleoproterozoic (ca. 2.3 Ga) sandstones and siltstones have initial <sup>187</sup>Os/<sup>188</sup>Os as high as 1.1 (34), which may represent an approximate upper limit for the <sup>187</sup>Os/<sup>188</sup>Os of the eroding upper continental crust at 2.5 Ga. The Os isotope mass balance equation for seawater can be represented by

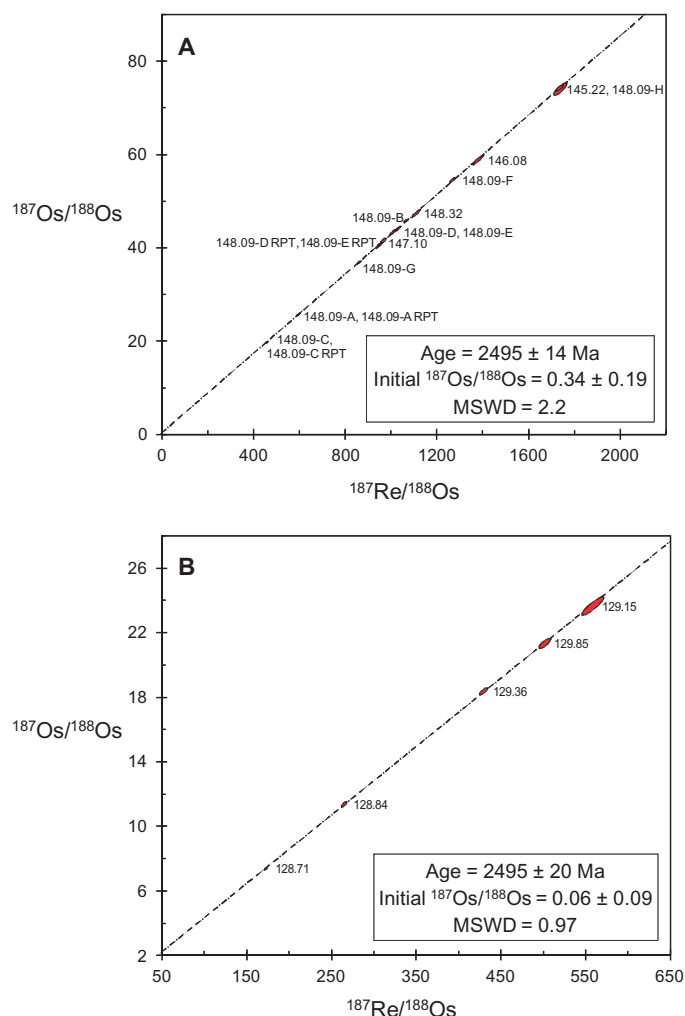
$$^{187}\text{Os}/^{188}\text{Os}_{\text{seawater}} = (f_{\text{continental}})(^{187}\text{Os}/^{188}\text{Os}_{\text{continental}}) + (f_{\text{mantle/extraterrestrial}})(^{187}\text{Os}/^{188}\text{Os}_{\text{mantle/extraterrestrial}})$$

where the *f* terms represent the relative fraction of Os input to seawater and *f*<sub>continental</sub> + *f*<sub>mantle/extraterrestrial</sub> = 1. The mantle and extraterrestrial (chondritic) contributions have similar <sup>187</sup>Os/<sup>188</sup>Os. This equation can be rearranged to obtain the continental flux of Os as follows

$$f_{\text{continental}} = (^{187}\text{Os}/^{188}\text{Os}_{\text{seawater}} - ^{187}\text{Os}/^{188}\text{Os}_{\text{mantle}}) / (^{187}\text{Os}/^{188}\text{Os}_{\text{continental}} - ^{187}\text{Os}/^{188}\text{Os}_{\text{mantle}})$$

Assuming a seawater <sup>187</sup>Os/<sup>188</sup>Os of 0.34 ± 0.19 (based on our data from the Mount McRae Shale), a mantle/extraterrestrial <sup>187</sup>Os/<sup>188</sup>Os of 0.11, and a continental <sup>187</sup>Os/<sup>188</sup>Os of 1.10, the continental flux represented ~5 to 40% of Os in Hamersley Basin seawater. A higher ratio of continental versus mantle/extraterrestrial inputs would occur if riverine <sup>187</sup>Os/<sup>188</sup>Os was less than 1.10.

A significant continental Os flux to seawater does not require high atmospheric O<sub>2</sub> concentrations because Os is a siderophile and chalcophile metal that resides primarily in easily weathered sulfide minerals. Subaerial oxidation of continental sulfide minerals is likely to be more efficient than submarine oxidative weathering within oxygenated surface waters along ocean margins (47). It has also been shown that oxidative dissolution of pyrite and molybdenite can potentially occur on geologically short time scales (tens of thousands of years or less) beneath an atmosphere containing sufficiently low O<sub>2</sub> concentrations (≤0.001% PAL) (9) to allow preservation of S-MIF signatures in sedimentary rocks (15, 48). However, atmospheric O<sub>2</sub> concentrations would likely need to reach ~0.03% PAL (this estimate has an order-of-magnitude uncertainty), at least locally, to allow efficient riverine transport of Os to seawater; otherwise, dissolved Os would have been reduced and removed to riverbeds and floodplains via redox reactions with Fe(II) (5, 49). Above this



**Fig. 2. Re-Os isochron diagrams for the Mount McRae Shale. (A)** Interval of 145.22 to 148.32 m in core ABDP-9. **(B)** Interval of 128.71 to 129.85 m in core ABDP-9. MSWD, mean square of weighted deviates. The age uncertainty includes the <sup>187</sup>Re decay constant uncertainty. RPT, replicate analysis.

atmospheric O<sub>2</sub> threshold, theoretical calculations indicate that Fe(II) should be efficiently oxidized to Fe(III) during continental weathering (5).

Recently, it has been hypothesized that localized (submeter scale) oxidative weathering environments associated with microbial mats in soils, rock surfaces, and sediments in lakes, rivers, and estuaries could permit the oxidative release of redox-sensitive trace metals and their transport to Archean oceans without any appreciable increase in atmospheric O<sub>2</sub> concentrations (50). Our data do not firmly rule out this hypothesis. However, because of the reactivity of Os with Fe(II), long-range transport of Os from a locally oxidizing weathering environment to an organic-rich sediment sink should require sufficiently high background atmospheric O<sub>2</sub> levels to allow for pervasive oxidation and removal of Fe(II) from meteoric waters. Thus, we suggest that the radiogenic seawater <sup>187</sup>Os/<sup>188</sup>Os captured by the black shales from 145.22 to 148.32 m is more easily explained if nontrivial amounts of O<sub>2</sub> (≥0.03% PAL) were present in the atmosphere because this allows efficient riverine transport of continental Os to seawater.

The S-MIF signatures at 145.22 to 148.32 m (2) do not disappear as expected if atmospheric O<sub>2</sub> concentrations were high enough to permit quantitative oxidation of Fe(II) in meteoric waters and thus efficient transport of dissolved Os by rivers. We suggest that the persistence of S-MIF signatures may result from propagation of a relict crustal signature (10). Alternatively, the atmospheric O<sub>2</sub> level required for widespread removal of dissolved Fe(II) from continental meteoric waters is overestimated. In any case, our data robustly point to oxidative mobilization of Os from Earth's crust followed by large-scale riverine transport of Os to the Hamersley Basin.

### Transient oxidative continental weathering at 2.5 Ga

In contrast to the 145.22- to 148.32-m interval, the black shales at 128.71 to 129.85 m yield an initial <sup>187</sup>Os/<sup>188</sup>Os of  $0.06 \pm 0.09$  (Fig. 2) that is statistically indistinguishable from the mantle/extraterrestrial value of ~0.11 (1), pointing to weak riverine transport of continental Os and associated oxidative continental weathering. The extreme opposite ends of the 2σ uncertainties of the initial <sup>187</sup>Os/<sup>188</sup>Os from 128.71 to 129.85 m ( $0.06 \pm 0.09$ ) and 145.22 to 148.32 m ( $0.34 \pm 0.19$ ) overlap, but an unpaired *t* test indicates that the initial <sup>187</sup>Os/<sup>188</sup>Os values from the two intervals are most likely different ( $P < 0.0001$ , two-tailed).

Stratigraphic trends in the initial <sup>187</sup>Os/<sup>188</sup>Os calculated for individual samples within the two stratigraphic intervals cannot be evaluated because the uncertainties of individual sample ratios (as determined by numerical error propagation of age, <sup>187</sup>Re decay constant, and present-day <sup>187</sup>Re/<sup>188</sup>Os and <sup>187</sup>Os/<sup>188</sup>Os uncertainties) are large and thus statistically overlap (table S1). This is a consequence of the old (late Archean) age of the Mount McRae Shale and its high present-day <sup>187</sup>Os/<sup>188</sup>Os ratios. In contrast, the initial <sup>187</sup>Os/<sup>188</sup>Os of Re-Os isochron regressions, defined by multiple samples, provide a more precise average estimate of seawater <sup>187</sup>Os/<sup>188</sup>Os for each stratigraphic interval. The statistically higher initial <sup>187</sup>Os/<sup>188</sup>Os for 145.22 to 148.32 m (compared with 128.71 to 129.85 m) indicates that the flux of radiogenic riverine Os to seawater became more prominent relative to the unradiogenic mantle/extraterrestrial flux at this time.

An alternative explanation for the higher seawater <sup>187</sup>Os/<sup>188</sup>Os at 145.22 to 148.32 m is a decreased flux of mantle/extraterrestrial Os to seawater, but we consider this scenario to be highly unlikely. The upper Mount McRae Shale (125 to 150 m in ABDP-9) was predominantly deposited from euxinic bottom waters based on Fe speciation data (Fig. 1) (15). Hence, the stratigraphic variations in Re and Mo concentrations likely reflect changes in seawater metal concentrations rather than variations in local bottom

water redox conditions. The highest Re and Mo concentrations are observed at 140 to 150 m in ABDP-9 (1) and cannot be explained by a decline in the mantle/extraterrestrial fluxes because such decreases should result in lower Re and Mo concentrations in black shales. Similarly, an increase in the mantle/extraterrestrial flux during deposition of the black shales above 140 m cannot account for the lower seawater <sup>187</sup>Os/<sup>188</sup>Os at 128.71 to 129.85 m because this scenario should result in an increase rather than a decrease in the Re and Mo concentrations. Hence, the decline in Re and Mo enrichments above 140 m in ABDP-9 is consistent with decreased oxidative weathering rates (1). Together, the high Re and Mo enrichments and elevated seawater <sup>187</sup>Os/<sup>188</sup>Os at 145.22 to 148.32 m point to a transient increase in oxidative continental weathering and likely atmospheric and surface ocean O<sub>2</sub> levels.

We emphasize that oxidative weathering was not necessarily negligible before and after this transient event. Concentrations of Mo and Re and Mo isotope compositions in black shales above 140 m and below 150-m depth in ABDP-9 are slightly elevated above continental values, suggesting weak oxidative weathering (1, 19). The main point is that the initial <sup>187</sup>Os/<sup>188</sup>Os data from 145.22 to 148.32 m indicate a significant temporal shift in the scale of oxidative continental weathering during deposition of the Mount McRae Shale. Therefore, the new Os isotope data highlight that the onset of oxygenesis, oxidative continental weathering, and Earth surface oxygenation was most likely a complex and dynamic process (7, 10).

Hence, our new Os isotope data for the 2.5-Ga Mount McRae Shale have profound implications for the nature of photosynthetic O<sub>2</sub> accumulation in Archean surface environments. Rather than linear stepwise increases in environmental O<sub>2</sub> levels, it is likely that transient oxygenation events were separated by intervals of less oxygenated conditions. Oscillation in O<sub>2</sub> levels driven by the combined effects of complex biospheric feedbacks and tectonic processes may have been particularly characteristic of the late Archean Eon. The frequency, magnitude, and duration of these transient environmental oxygenation events may have increased through time—culminating in the early Paleoproterozoic Great Oxidation Event.

## MATERIALS AND METHODS

### Rhenium-osmium isotope analyses

The Re-Os analyses were carried out at the Canadian Centre for Isotopic Microanalysis, Department of Earth and Atmospheric Sciences, University of Alberta. Eight samples of finely laminated homogeneous black shale containing disseminated pyrite (but not macroscopic pyrite nodules) were selected from a depth of 148.09 to 148.15 m. Each sample (comprising 15 to 25 g) was ground to remove cutting and drilling marks, broken into chips using metal-free methods, and powdered in an agate mill. About ~0.2 g of sample powder and a known amount of <sup>185</sup>Re-<sup>190</sup>Os spike solution were digested in 8 ml of a Cr<sup>VI</sup>-H<sub>2</sub>SO<sub>4</sub> solution for 48 hours at 200°C in sealed Carius tubes (51). Multiple studies have demonstrated that the Cr<sup>VI</sup>-H<sub>2</sub>SO<sub>4</sub> solution minimizes the dissolution of detrital Os from silicate minerals, whereas the organic matter and sulfide minerals are digested, thus releasing hydrogenous Re and Os into the solution (38, 51–53).

After digestion, Os was separated from the Cr<sup>VI</sup>-H<sub>2</sub>SO<sub>4</sub> solution by solvent extraction into chloroform and further purified by extraction into concentrated HBr, followed by double microdistillation (54, 55). An aliquot (2 ml) of the Cr<sup>VI</sup>-H<sub>2</sub>SO<sub>4</sub> solution was taken and mixed with 15 ml of 5 N NaOH and 15 ml of acetone to separate Re by solvent



extraction into acetone. The acetone fraction was dried and then further purified for Re using anion exchange chromatography (51). The purified Re and Os cuts were loaded onto Ni and Pt filaments, respectively, and analyzed for their isotopic composition by isotope dilution–negative thermal ionization mass spectrometry on a Thermo Triton (38, 56). In-house standard solutions yielded average  $^{185}\text{Re}/^{187}\text{Re}$  and  $^{187}\text{Os}/^{188}\text{Os}$  isotope ratios of  $0.59778 \pm 0.00077$  ( $1\sigma$ ) and  $0.10684 \pm 0.00015$  ( $1\sigma$ ), respectively, which are in excellent agreement with previous studies (38, 56). Total procedural blanks for Re and Os were 15 and 0.3 pg, respectively, with a blank  $^{187}\text{Os}/^{188}\text{Os}$  of 0.20.

### Statistical analysis

Regression of Re–Os isotope data was carried out using K. Ludwig's Microsoft Excel add-in program *Isoplot* 4.15 (Berkeley Geochronology Center) using a  $^{187}\text{Re}$  decay constant of  $1.666 \times 10^{-11} \text{ year}^{-1}$  (57, 58), calculated  $2\sigma$  uncertainties for sample  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  as determined by numerical error propagation, and the error correlation ( $\rho$ ) between the isotope ratios. The  $2\sigma$  age uncertainty includes the  $^{187}\text{Re}$  decay constant uncertainty of  $\pm 0.31\%$  (57).

### Further analysis of the Re–Os isotope systematics in the Mount McRae Shale

Previously, a Re–Os isochron age of  $2501.1 \pm 8.2 \text{ Ma}$  (MSWD = 1.1; the uncertainty on the  $^{187}\text{Re}$  decay constant was not included) and an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.04 \pm 0.06$  were obtained for the Mount McRae Shale in ABDP-9 (1). This isochron regression was derived by combining five analyses from 128.71 to 129.85 m and four analyses from 145.22 to 148.32 m. Although the  $2501.1 \pm 8.2 \text{ Ma}$  date is in excellent agreement with U–Pb zircon depositional age constraints for the Mount McRae Shale (32), the initial  $^{187}\text{Os}/^{188}\text{Os}$  is lower than the mantle/chondritic value of 0.11 at 2.5 Ga (1).

Our new Re–Os analyses shed insight on the origin of the subchondritic initial  $^{187}\text{Os}/^{188}\text{Os}$  of the original regression. The new initial  $^{187}\text{Os}/^{188}\text{Os}$  for the 145.22- to 148.32-m interval ( $0.34 \pm 0.19$ ) is now statistically higher (based on an unpaired  $t$  test) than the initial  $^{187}\text{Os}/^{188}\text{Os}$  derived from regression of the 128.71- to 129.85-m interval ( $0.06 \pm 0.09$ ). Hence, combining the analyses from 128.71 to 129.85 m and 145.22 to 148.32 m violates the basic geochronology requirement that all samples have the same initial  $^{187}\text{Os}/^{188}\text{Os}$ . The original four analyses from 145.22 to 148.32 m have higher present-day  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  isotope ratios and yielded a higher initial  $^{187}\text{Os}/^{188}\text{Os}$  compared with the 128.71- to 129.85-m interval. Consequently, the effect of combining data from the two depth intervals is a slightly steeper slope (which translates into a slightly higher nominal age relative to individual regressions of the two depth intervals) and an erroneously low initial  $^{187}\text{Os}/^{188}\text{Os}$ .

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/1/10/e1500777/DC1>

Table S1. Re–Os abundance and isotope data for the Mount McRae Shale, Western Australia (drill core ABDP-9).

### REFERENCES AND NOTES

1. A. D. Anbar, Y. Duan, T. W. Lyons, G. L. Arnold, B. Kendall, R. A. Creaser, A. J. Kaufman, G. W. Gordon, C. Scott, J. Garvin, R. Buick, A whiff of oxygen before the Great Oxidation Event? *Science* **317**, 1903–1906 (2007).

2. A. J. Kaufman, D. T. Johnston, J. Farquhar, A. L. Masterson, T. W. Lyons, S. Bates, A. D. Anbar, G. L. Arnold, J. Garvin, R. Buick, Late Archean biospheric oxygenation and atmospheric evolution. *Science* **317**, 1900–1903 (2007).
3. B. Kendall, C. T. Reinhard, T. W. Lyons, A. J. Kaufman, S. W. Poulton, A. D. Anbar, Pervasive oxygenation along late Archaean ocean margins. *Nat. Geosci.* **3**, 647–652 (2010).
4. A. D. Czaja, C. M. Johnson, E. E. Roden, B. L. Beard, A. R. Voegelin, T. F. Nägler, N. J. Beukes, M. Wille, Evidence for free oxygen in the Neoproterozoic ocean based on coupled iron–molybdenum isotope fractionation. *Geochim. Cosmochim. Acta* **86**, 118–137 (2012).
5. S. A. Crowe, L. N. Dossing, N. J. Beukes, M. Bau, S. J. Kruger, R. Frei, D. E. Canfield, Atmospheric oxygenation three billion years ago. *Nature* **501**, 535–538 (2013).
6. N. J. Planavsky, D. Asael, A. Hofmann, C. T. Reinhard, S. V. Lalonde, A. Knudsen, X. Wang, F. Ossa Ossa, E. Pecoits, A. J. B. Smith, N. J. Beukes, A. Bekker, T. M. Johnson, K. O. Konhauser, T. W. Lyons, O. J. Rouxel, Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. *Nat. Geosci.* **7**, 283–286 (2014).
7. T. W. Lyons, C. T. Reinhard, N. J. Planavsky, The rise of oxygen in Earth's early ocean and atmosphere. *Nature* **506**, 307–315 (2014).
8. J. Farquhar, H. Bao, M. Thiemens, Atmospheric influence of Earth's earliest sulfur cycle. *Science* **289**, 756–758 (2000).
9. A. A. Pavlov, J. F. Kasting, Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic Archean atmosphere. *Astrobiology* **2**, 27–41 (2002).
10. C. T. Reinhard, N. J. Planavsky, T. W. Lyons, Long-term sedimentary recycling of rare sulphur isotope anomalies. *Nature* **497**, 100–103 (2013).
11. S. D. Domagal-Goldman, J. F. Kasting, D. T. Johnston, J. Farquhar, Organic haze, glaciations and multiple sulfur isotopes in the Mid-Archean Era. *Earth Planet. Sci. Lett.* **269**, 29–40 (2008).
12. A. L. Zerkle, M. W. Claire, S. D. Domagal-Goldman, J. Farquhar, S. W. Poulton, A bistable organic-rich atmosphere on the Neoproterozoic Earth. *Nat. Geosci.* **5**, 359–363 (2012).
13. F. Kurzwil, M. Claire, C. Thomazo, M. Peters, M. Hannington, H. Strauss, Atmospheric sulfur rearrangement 2.7 billion years ago: Evidence for oxygenic photosynthesis. *Earth Planet. Sci. Lett.* **366**, 17–26 (2013).
14. M. W. Claire, J. F. Kasting, S. D. Domagal-Goldman, E. E. Stüeken, R. Buick, V. S. Meadows, Modeling the signature of sulfur mass-independent fractionation produced in the Archean atmosphere. *Geochim. Cosmochim. Acta* **141**, 365–380 (2014).
15. C. T. Reinhard, R. Raiswell, C. Scott, A. D. Anbar, T. W. Lyons, A late Archean sulfidic sea stimulated by early oxidative weathering of the continents. *Science* **326**, 713–716 (2009).
16. B. B. Sageman, A. E. Murphy, J. P. Werne, C. A. Ver Straeten, D. J. Hollander, T. W. Lyons, A tale of shales: The relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian basin. *Chem. Geol.* **195**, 229–273 (2003).
17. T. W. Lyons, M. Kashgarian, Paradigm lost, paradigm found: The Black Sea–black shale connection as viewed from the anoxic basin margin. *Oceanography* **18**, 86–99 (2005).
18. J. Garvin, R. Buick, A. D. Anbar, G. L. Arnold, A. J. Kaufman, Isotopic evidence for an aerobic nitrogen cycle in the latest Archean. *Science* **323**, 1045–1048 (2009).
19. Y. Duan, A. D. Anbar, G. L. Arnold, T. W. Lyons, G. W. Gordon, B. Kendall, Molybdenum isotope evidence for mild environmental oxygenation before the Great Oxidation Event. *Geochim. Cosmochim. Acta* **74**, 6655–6668 (2010).
20. B. Kendall, G. A. Brennecke, S. Weyer, A. D. Anbar, Uranium isotope fractionation suggests oxidative uranium mobilization at 2.50 Ga. *Chem. Geol.* **362**, 105–114 (2013).
21. E. E. Stüeken, R. Buick, A. D. Anbar, Selenium isotopes support free  $\text{O}_2$  in the latest Archean. *Geology* **43**, 259–262 (2015).
22. W. W. Fischer, S. Slotznick, J. E. Johnson, S. M. Webb, B. Rasmussen, T. D. Raub, J. L. Kirschvink, Archean 'whiffs of oxygen' tied to post-depositional processes, paper presented at the Goldschmidt Conference, Sacramento, CA, 8 to 13 June 2014.
23. G. Ravizza, K. K. Turekian, Application of the  $^{187}\text{Re}/^{187}\text{Os}$  system to black shale geochronometry. *Geochim. Cosmochim. Acta* **53**, 3257–3262 (1989).
24. A. S. Cohen, A. L. Coe, J. M. Bartlett, C. J. Hawkesworth, Precise Re–Os ages of organic-rich mudrocks and the Os isotope composition of Jurassic seawater. *Earth Planet. Sci. Lett.* **167**, 159–173 (1999).
25. S. Levasseur, J.-L. Birck, C. J. Allègre, Direct measurement of femtomoles of osmium and the  $^{187}\text{Os}/^{186}\text{Os}$  ratio in seawater. *Science* **282**, 272–274 (1998).
26. O. B. Woodhouse, G. Ravizza, K. K. Falkner, P. J. Statham, B. Peucker-Ehrenbrink, Osmium in seawater: Vertical profiles of concentration and isotopic composition in the eastern Pacific Ocean. *Earth Planet. Sci. Lett.* **173**, 223–233 (1999).
27. S. Levasseur, J.-L. Birck, C. J. Allègre, The osmium riverine flux and the oceanic mass balance of osmium. *Earth Planet. Sci. Lett.* **174**, 7–23 (1999).
28. B. Peucker-Ehrenbrink, Accretion of extraterrestrial matter during the last 80 million years and its effect on the marine osmium isotope record. *Geochim. Cosmochim. Acta* **60**, 3187–3196 (1996).
29. R. R. Cave, G. E. Ravizza, C. R. German, J. Thomson, R. W. Nesbitt, Deposition of osmium and other platinum-group elements beneath the ultramafic-hosted Rainbow hydrothermal plume. *Earth Planet. Sci. Lett.* **210**, 65–79 (2003).

30. M. Sharma, E. J. Rosenberg, D. A. Butterfield, Search for the proverbial mantle osmium sources to the oceans: Hydrothermal alteration of mid-ocean ridge basalt. *Geochim. Cosmochim. Acta* **71**, 4655–4667 (2007).
31. G. Ravizza, K. K. Turekian, The osmium isotopic composition of organic-rich marine sediments. *Earth Planet. Sci. Lett.* **110**, 1–6 (1992).
32. B. Rasmussen, T. S. Blake, I. R. Fletcher, U-Pb zircon age constraints on the Hamersley spherule beds: Evidence for a single 2.63 Ga Jeerinah-Carawine impact ejecta layer. *Geology* **33**, 725–728 (2005).
33. B. Rasmussen, I. R. Fletcher, S. Sheppard, Isotopic dating of the migration of a low-grade metamorphic front during orogenesis. *Geology* **33**, 773–776 (2005).
34. Y. Sekine, K. Suzuki, R. Senda, K. T. Goto, E. Tajika, R. Tada, K. Goto, S. Yamamoto, N. Ohkouchi, N. O. Ogawa, T. Maruoka, Osmium evidence for synchronicity between a rise in atmospheric oxygen and Palaeoproterozoic deglaciation. *Nat. Commun.* **2**, 502 (2011).
35. J. L. Hannah, A. Bekker, H. J. Stein, R. J. Markey, H. D. Holland, Primitive Os and <sup>2316</sup>Ma age for marine shale: Implications for Paleoproterozoic glacial events and the rise of atmospheric oxygen. *Earth Planet. Sci. Lett.* **225**, 43–52 (2004).
36. J. L. Hannah, H. J. Stein, A. Zimmerman, G. Yang, R. J. Markey, V. A. Melezhik, Precise 2004 ± 9 Ma Re–Os age for Pechenga black shale: Comparison of sulfides and organic material. *Geochim. Cosmochim. Acta* **70**, A228 (2006).
37. G. Yang, J. L. Hannah, A. Zimmerman, H. J. Stein, A. Bekker, Re–Os depositional age for Archean carbonaceous slates from the southwestern Superior Province: Challenges and insights. *Earth Planet. Sci. Lett.* **280**, 83–92 (2009).
38. B. Kendall, D. van Acken, R. A. Creaser, Depositional age of the early Paleoproterozoic Klipputs Member, Nelani Formation (Ghaap Group, Transvaal Supergroup, South Africa) and implications for low-level Re–Os geochronology and Paleoproterozoic global correlations. *Precambrian Res.* **237**, 1–12 (2013).
39. J. Golden, M. McMillan, R. T. Downs, G. Hystad, I. Goldstein, H. J. Stein, A. Zimmerman, D. A. Sverjensky, J. T. Armstrong, R. M. Hazen, Rhenium variations in molybdenite (MoS<sub>2</sub>): Evidence for progressive subsurface oxidation. *Earth Planet. Sci. Lett.* **366**, 1–5 (2013).
40. R. M. Morelli, R. A. Creaser, D. Selby, K. D. Kelley, D. L. Leach, A. R. King, Re–Os sulfide geochronology of the Red Dog sediment-hosted Zn–Pb–Ag deposit, Brooks Range, Alaska. *Econ. Geol.* **99**, 1569–1576 (2004).
41. R. M. Morelli, C. C. Bell, R. A. Creaser, A. Simonetti, Constraints on the genesis of gold mineralization at the Homestake gold deposit, Black Hills, South Dakota from rhenium–osmium sulfide geochronology. *Miner. Deposita* **45**, 461–480 (2010).
42. C. A. Miller, B. Peucker-Ehrenbrink, B. D. Walker, F. Marcantonio, Re-assessing the surface cycling of molybdenum and rhenium. *Geochim. Cosmochim. Acta* **75**, 7146–7179 (2011).
43. A. Dubin, B. Peucker-Ehrenbrink, The importance of organic-rich shales to the geochemical cycles of rhenium and osmium. *Chem. Geol.* **403**, 111–120 (2015).
44. R. M. Hazen, R. C. Ewing, D. A. Sverjensky, Evolution of uranium and thorium minerals. *Amer. Mineral.* **94**, 1293–1311 (2009).
45. D. A. Sverjensky, N. Lee, The Great Oxidation Event and mineral diversification. *Elements* **6**, 31–36 (2010).
46. B. Dhuime, C. J. Hawkesworth, P. A. Cawood, C. D. Storey, A change in the geodynamics of continental growth 3 billion years ago. *Science* **335**, 1334–1336 (2012).
47. C. T. Reinhard, S. V. Lalonde, T. W. Lyons, Oxidative sulfide dissolution on the early Earth. *Chem. Geol.* **362**, 44–55 (2013).
48. N. D. Greber, U. Mäder, T. F. Nägler, Experimental dissolution of molybdenum-sulphides at low oxygen concentrations: A first-order approximation of late Archean atmospheric conditions. *Earth Space Sci.* **2**, 173–180 (2015).
49. B. Kendall, An osmium-based method for assessing the source of dissolved rhenium and molybdenum to Archean seawater. *Chem. Geol.* **385**, 92–103 (2014).
50. S. V. Lalonde, K. O. Konhauser, Benthic perspective on Earth's oldest evidence for oxygenic photosynthesis. *Proc. Natl. Acad. Sci. U.S.A.* **112**, 995–1000 (2015).
51. D. Selby, R. A. Creaser, Re–Os geochronology of organic rich sediments: An evaluation of organic matter analysis methods. *Chem. Geol.* **200**, 225–240 (2003).
52. B. S. Kendall, R. A. Creaser, G. M. Ross, D. Selby, Constraints on the timing of Marinoan “Snowball Earth” glaciation by <sup>187</sup>Re–<sup>187</sup>Os dating of a Neoproterozoic, post-glacial black shale in Western Canada. *Earth Planet. Sci. Lett.* **222**, 729–740 (2004).
53. A. D. Rooney, D. M. Chew, D. Selby, Re–Os geochronology of the Neoproterozoic–Cambrian Dalradian Supergroup of Scotland and Ireland: Implications for Neoproterozoic stratigraphy, glaciations and Re–Os systematics. *Precambrian Res.* **185**, 202–214 (2011).
54. A. S. Cohen, F. G. Waters, Separation of osmium from geological materials by solvent extraction for analysis by thermal ionisation mass spectrometry. *Anal. Chim. Acta* **332**, 269–275 (1996).
55. J. L. Birck, M. R. Barman, F. Capmas, Re–Os isotopic measurements at the femtomole level in natural samples. *Geostand. Geoanal. Res.* **21**, 19–27 (1997).
56. D. van Acken, D. Thomson, R. H. Rainbird, R. A. Creaser, Constraining the depositional history of the Neoproterozoic Shaler Supergroup, Amundsen Basin, NW Canada: Rhenium–osmium dating of black shales from the Wynniatt and Boot Inlet Formations. *Precambrian Res.* **236**, 124–131 (2013).
57. M. I. Smoliar, R. J. Walker, J. W. Morgan, Re–Os ages of group IIA, IIIA, IVA, and IVB iron meteorites. *Science* **271**, 1099–1102 (1996).
58. D. Selby, R. A. Creaser, H. J. Stein, R. J. Markey, J. L. Hannah, Assessment of the <sup>187</sup>Re decay constant by cross calibration of Re–Os molybdenite and U–Pb zircon chronometers in magmatic ore systems. *Geochim. Cosmochim. Acta* **71**, 1999–2013 (2007).
59. S. W. Poulton, D. E. Canfield, Ferruginous conditions: A dominant feature of the ocean through Earth's history. *Elements* **7**, 107–112 (2011).
60. R. Raiswell, C. T. Reinhard, A. Derkowski, J. Owens, S. H. Bottrell, A. D. Anbar, T. W. Lyons, Formation of syngenetic and early diagenetic iron minerals in the late Archean Mt. McRae Shale, Hamersley Basin, Australia: New insights on the patterns, controls and paleo-environmental implications of authigenic mineral formation. *Geochim. Cosmochim. Acta* **75**, 1072–1087 (2011).

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